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Cadmium Analysis by Radiochemical Neutron Activation Analysis

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Radiochemical neutron activation analysis (RNAA) has been routinely used at the National Bureau of Standards to analyze Cd in a variety of environmentally important matrices. The method used to separate Cd from other neutron-activated products is solvent extraction. Zinc diethyldithiocarbamate [$Zn(DDC)_2$] in chloroform will quantitatively extract Cd from an aqueous solution over a pH range from 1 to 12. In addition to the extraction of Cd, $Zn(DDC)_2$ will also extract Cu, which can interfere with the Cd analysis by producing a high background level of radiation. This can be avoided by first extracting with $Bi(DDC)_3$ in chloroform which removes Cu, but not Cd. Copper concentrations can, therefore, be determined in addition to Cd.

This two extraction radiochemical separation procedure is very versatile and is often used as part of a larger multi-element analysis scheme. One such scheme involves the use of an inorganic-ion exchanger, Hydrated Manganese Dioxide (HMD), to retain As, Sb, Se, and Cr prior to extraction. The eluted fraction is then extracted with $Bi(DDC)_3$ to remove Cu, and then with $Zn(DDC)_2$ to remove Cd.

Cadmium has been suspected of causing detrimental health effects in humans even at very low levels (*1*). Since Cd is commonly found at the trace or ultra-trace level, many analytical techniques do not have the sensitivity to accurately determine the concentration of this element in many environmentally important materials. In a recent interlaboratory comparison of oyster material carried out by the International Atomic Energy Agency, the reported values of the Cd concentration ranged from 0.4 to 4.4 μg/g (*2*). This illustrates the problems involved in determining the "true" Cd concentration in biological materials even when this concentration is relatively high; these problems become more serious as the Cd content decreases. In addition, there are some instances in which the total amount of material available for analysis is very small, such as for hair samples or certain types of atmospheric particulate samples. Analytical techniques capable of measuring very small amounts of Cd are therefore required.

Radiochemical neutron activation analysis (RNAA) has been routinely used at the National Bureau of Standards to determine Cd in a variety of matrices. RNAA offers the advantages of high sensitivity, excellent selectivity, and no chemical blank. Furthermore, the ability to add carriers during the chemical dissolution and separation enables quantitative recovery of the element.

Basically, neutron activation analysis involves the irradiation of a sample and standard with neutrons, usually in a nuclear reactor, to form radioactive isotopes. As these radioisotopes decay, many of them emit γ-rays with energies characteristic of the nuclide (element) emitting them. The quantitative measurement of an element can be obtained by comparing the intensity of the appropriate γ radiation emitted by a sample, with a standard containing a known amount of the element of interest.

The concentrations of many elements can be determined instrumentally—that is, without separating them from the neutron-activated matrix. Cadmium, however, usually has to be determined radiochemically, or isolated from other neutron-activated products, due to the high background level of radiation produced by certain other radioactive nuclides. Many different types of radiochemical separations can be used for RNAA such as: solvent extraction, distillation, precipita-

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tion, ion-exchange chromatography, or electrodeposition. The method we use to isolate Cd is solvent extraction (*3-4*). Zinc diethyldithiocarbamate [$Zn(DDC)_2$] in chloroform will quantitatively extract Cd from an aqueous solution over a pH range of from 1 to 12.

In addition to Cd, $Zn(DDC)_2$ also extracts Cu (*5*). In many matrices, Cu can interfere with the determination of Cd by producing a high background level of radiation. This problem can be eliminated by first extracting with bismuth diethyldithiocarbamate [$Bi(DDC)_3$] in chloroform, which removes Cu but not Cd. Cu can then also be determined if desired.

Experimental

Preparation of Metal DDC Compounds

The $Zn(DDC)_2$ and $Bi(DDC)_3$ compounds which were used for analysis were prepared by mixing aqueous solutions of NaDDC and either $Zn(NO_3)_2$ or $Bi(NO_3)_3$. The $M(DDC)_x$ compound formed was insoluble in water and precipitated. The precipitate was filtered, washed with water, and dissolved in chloroform. An equal volume of ethanol was added to the solution, which was then set aside to allow the chloroform to evaporate at room temperature. After the chloroform evaporated, the $M(DDC)_x$ compound crystallized in the remaining ethanol. The crystals were filtered and allowed to dry at room temperature.

Procedure

The samples and primary standards were sealed in cleaned quartz vials and irradiated together in the NBS reactor at a thermal neutron flux of 5×10^{13} n/cm^2-sec. Irradiation times of from 1 to 4 hr were used. The primary standards consisted of a solution prepared from high purity metals dissolved in NBS high purity HNO_3 (*6*).

After irradiation, the samples were allowed to decay for 3 days after which they were weighed and transferred to dissolution vessels. Three types of vessels were used depending on the matrix: Erlenmeyer flasks, Teflon wet-ashing vessels, and a Teflon-lined bomb. Copper and Cd carriers (approximately 100 μg each) were added to each vessel and the samples were dissolved. Various acid mixtures were used, including HNO_3 alone, HNO_3–H_2SO_4, and HNO_3–$HClO_4$ (not in the bomb). If silica was present, some HF was also added.

After dissolution, 100 mg of Zn^{+2} hold-back carrier was added to minimize exchange between the radioactive Zn of the samples, and the organic Zn of the $Zn(DDC)_2$ solution used to extract the Cd. The pH of each solution was adjusted to 1.5 with NH_4OH and the volume brought to about 60 ml with deionized water. Each solution was then transferred to a 125 ml separatory funnel and shaken for 30 min with 20 ml of 0.003*M* $Bi(DDC)_3$ in chloroform using a shaking machine. The organic fraction containing Cu was drained into a 120 ml polyethylene bottle and the aqueous phase was washed for 15 sec with an additional 10 ml of the $Bi(DDC)_3/CHCl_3$ solution. The wash was then combined with the first $Bi(DDC)_3$ fraction and retained for counting.

A 20-ml portion of 0.005*M* $Zn(DDC)_2$ in chloroform was then added to the aqueous phase still in the separatory funnel, which was then shaken for 5 min. The organic fraction was drained into a second 120 ml polyethylene bottle, and the aqueous phase washed for 15 sec with an additional 10 ml of the $Zn(DDC)_2/CHCl_3$ solution. The wash was combined with the first $Zn(DDC)_2$ fraction which was retained for counting.

Two different procedures were followed for the standards. One standard was prepared by pipetting a known amount of irradiated solution into a dissolution vessel with carriers and some unirradiated sample material. This material was dissolved in the same manner as were the samples used for analysis. A second standard was pipetted directly into 1*M* HNO_3 along with carriers. Both standards were then subjected to the same separation scheme used for the samples.

Counting

The samples and standards were counted on Ge(Li) detectors with active volumes of from 60 to 75 cm^3 coupled to 4096 channel pulse height analyzer systems. The $Bi(DDC)_3$ solutions containing Cu were counted immediately after separation. The 511 keV peak produced by the annihilation of positrons emitted by ^{64}Cu was used for analysis.

The $Zn(DDC)_2$ solutions containing Cd were allowed to decay for at least 24 hr to establish the equilibrium between ^{115}Cd and its daughter ^{115m}In. The 336 keV line from ^{115m}In, and the 527 keV line from ^{115}Cd were both used for analysis. Computer code QLN1 (*7*) was used for data reduction supplemented by hand integrations of poorly defined peaks.

Results and Discussion

A number of National Bureau of Standards Standard Reference Materials (SRMs) were analyzed by the above procedure, and the Cd and Cu results

Table 1. Cadmium in various SRMs.

	Cd concentration, μg/g	
	This work	Certified
Orchard leaves (SRM 1571)	0.116 ± 0.008	0.11 ± 0.01
Pine needles (SRM 1575)	0.194 ± 0.009	< 0.5
Bovine liver (SRM 1577)	0.295 ± 0.015	0.27 ± 0.04
Rice flour (SRM 1568)	0.029 ± 0.005	0.029 ± 0.004
Wheat flour (SRM 1567)	0.030 ± 0.005	0.032 ± 0.007
Subbituminous coal (SRM 1635)	0.030 ± 0.002	0.03 ± 0.01
River sediment (SRM 1645)	10.2 ± 0.4	10.2 ± 1.5
Urban particulate (SRM 1648)	71.2 ± 3.7	74 ± 7

Table 2. Copper in various SRMs.

	Cu concentration, μg/g	
	This work	Certified
Orchard leaves (SRM 1571)	11.6 ± 0.4	12 ± 1
Pine needles (SRM 1575)	3.04 ± 0.16	3.0 ± 0.3
Bovine liver (SRM 1577)	185 ± 7	193 ± 10
Rice flour (SRM 1568)	2.12 ± 0.09	2.2 ± 0.3
Wheat flour (SRM 1567)	2.21 ± 0.10	2.0 ± 0.3
Subbituminous Coal (SRM 1635)	3.56 ± 0.18	3.6 ± 0.3

Table 3. Orchard leaves (SRM 1571).

	Metal concentration, μg/g	
	This work	Certified
As	9.7 ± 0.4	10 ± 2
Sb	2.8 ± 0.1	2.9 ± 0.3
Se	0.09 ± 0.01	0.08 ± 0.01
Cr	2.67 ± 0.15	2.6 ± 0.3
Cd	0.116 ± 0.008	0.11 ± 0.01
Cu	11.6 ± 0.4	12 ± 1

Table 4. Subbituminous coal (SRM 1635).

	Metal concentration, μg/g	
	This work	Certified
As	0.44 ± 0.05	0.42 ± 0.15
Sb	0.12 ± 0.01	(0.14)[a]
Se	0.82 ± 0.04	0.9 ± 0.3
Cr	2.48 ± 0.08	2.5 ± 0.3
Cd	0.030 ± 0.002	0.03 ± 0.01
Cu	3.56 ± 0.18	3.6 ± 0.3

[a] Values in parentheses are NBS information only values.

Table 5. Bovine liver (SRM 1577).

	Metal concentration, μg/g	
	This work	Certified
As	0.054 ± 0.004	(0.055)[a]
Sb	0.010 ± 0.002	—
Se	1.06 ± 0.06	1.1 ± 0.1
Cr	0.085 ± 0.009	0.088 ± 0.012
Cd	0.295 ± 0.015	0.27 ± 0.04
Cu	185 ± 7	193 ± 10

[a] Values in parentheses are NBS information only values.

obtained are compared with the certified values in Tables 1 and 2. Very good agreement is observed, demonstrating the accuracy of this technique.

This two extraction radiochemical separation scheme is very versatile and can be used as a part of a larger multi-element analysis scheme. One such scheme used at NBS involves the use of an inorganic ion-exchanger, HMD (Hydrated Manganese Dioxide) (*8*, *9*) prior to the extractions. HMD will quantitatively retain As, Sb, Se, and Cr from a 1*M* HNO_3 solution. To perform this separation we normally dissolve the sample in HNO_3 + $HClO_4$ with some HF if silica is present. The samples are heated to incipient dryness and then brought to a volume of 20 ml with 1*M* HNO_3. The solutions are passed through plastic chromatographic columns, each containing a bed of HMD 7 mm by 30 mm. The columns are washed twice with 1*M* HNO_3 and dismantled for counting. Under these conditions Cu and Cd are completely eluted. The eluted fraction is then subjected to the two extraction procedure described above. Various SRMs were analyzed using this procedure and the results obtained are compared with the certified values in Tables 3–5. Very good agreement was obtained.

Conclusions

The two extraction radiochemical separation scheme for Cu and Cd described in this paper is both highly selective and extremely sensitive. The simplicity of the method allows a quantitative recovery of both elements, thus avoiding a calculation of chemical yield which can increase the analytical error. Furthermore, a relatively short time is required to carry out the complete procedure.

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